



Solvent extraction and self-assembly of nanosized aggregates of *p*-tert-butyl thiacalix[4]arenes tetrasubstituted at the lower rim by tertiary amide groups and monocharged metal cations in the organic phase

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ABSTRACT

New *p*-tert-butyl thiacalix[4]arenes functionalized with morpholide and pyrrolidide groups at the lower rim in *cone*, *partial cone*, and *1,3-alternate* conformations were synthesized, and their receptor properties for monocharged cations (alkali metal and silver ions) were studied using the picrate extraction method and dynamic light scattering (DLS). To evaluate the ability of the *p*-tert-butyl thiacalix[4]arene derivatives to recognize metal ions, liquid–liquid extraction of their picrate salts has been carried out in a mutually saturated water–dichloromethane system. The degrees of extraction and the extraction constants for monocharged metal cations (Li^+ , Na^+ , K^+ , Cs^+) have been determined. The ability of the systems, consisting of host and guest molecules, to self-assembly was proved by DLS using a Zetasizer Nano ZS particle size analyzer. It was shown that all the investigated thiacalix[4]arenes are able to form nanoscale particles with silver cations under the experimental conditions. The pyrrolidide derivative in the *cone* conformation showed both self-association and aggregation processes with lithium cations. The degree of extraction for all the investigated systems that formed nanoscale aggregates in the organic phase was more than 67% and the extraction constants, $\log K_{\text{ex}}$ determined by the picrate extraction method, more than 6.

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1. Introduction

The synthesis of nanoscale architectures and appropriate ‘smart’ materials devoted to creating molecular machines, information coding devices, electromechanical keys and sensors is considered nowadays as one of the perspective tendencies of the investigations into supramolecular chemistry. The development of supramolecular structures and nanoscale elements from single molecules is mainly based on self-assembly principles.¹ They assume spontaneous association of a number of relatively simple subunits, like single molecules, into a highly complex supramolecular product of defined structure. The sedimentation of atoms or molecules onto the surface followed by their self-ordering can be also used for these purposes.² It is necessary to mention that self-assembly processes are directed by weak reversible interactions, e.g., hydrogen bonding or van der Waals interactions. They provide thermodynamic control of the reaction with simultaneous correction of the product structural defects. As a result, equilibrium

structures are obtained without any intentional control of the process.²

Metal based supramolecular structures can be most effectively obtained by non-covalent self-assembly based on specially designed ligands to be spontaneously connected by metal ions.^{3–6} This makes it possible to combine the conformation lability of the ligand with the electrostatic interactions of the metal ions. The organic compounds able to form these structures recognize certain types of substrate, and provide the necessary special arrangement of their structural fragments, coordinative centers, and functional groups. Metal ions involved in such interactions act as coordinative centers that definitely direct the ligand surroundings. In addition, metal ion promotion of self-assembling is reversible and allows switching of the direction of the process from assembly to disassembly and vice versa in accordance with outside conditions.

This combination of the properties of the components is favorable for the synthesis of supramolecular structures with a high degree of symmetry, i.e., molecular triangles, squares, pentagons, hexagons, and even a three-dimensional octahedron.²

One of the most productive approaches to the development of the above receptor structures designed for the selective interaction with some substrates consists of the modification of the appropriate

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